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88361
S/195/60/001/004/009/015
B017/E055

AUTHORS: Popovskiy, V. V., Boreskov, G. K.

TITLE: Kinetics of the Isotopic Exchange Between Molecular Oxygen and Oxygen at the Surfaces of Iron, Cobalt, Nickel, and Copper Oxides

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 4, pp. 566-575

TEXT: The kinetics of the isotopic exchange between molecular oxygen and oxygen at the surfaces of iron, cobalt, nickel, and copper oxides were investigated. The measurements were made statically by using the continuous-flow apparatus shown schematically in Fig. 1. Oxygen containing an excess of O^{18} was prepared by electrolysis of water containing 4 at% O^{18} . The specific surfaces of the oxide catalysts were determined by the BET method.

The following values were found: Co_3O_4 : $7.7 \text{ m}^2/\text{g}$; Fe_2O_3 : $27.2 \text{ m}^2/\text{g}$; NiO : $7.8 \text{ m}^2/\text{g}$; CuO : $17.6 \text{ m}^2/\text{g}$. The exchange of oxygen between molecular oxygen and solid oxides at 10 - 30 mm Hg and 100 - 400°C is a complex

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Molecular Oxygen and Oxygen at the Surfaces of
Iron, Cobalt, Nickel, and Copper Oxides

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process. The Fe_2O_3 surface is homogeneous with respect to the exchange reaction, while the surfaces of Co_3O_4 , NiO and CuO are inhomogeneous in this respect. The isotopic exchange of oxygen with Fe_2O_3 , NiO , and CuO is illustrated in Table 1. A graphic representation of isotopic exchange as a function of time is given in Figs. 2-5. The kinetics of the exchange between gaseous oxygen and oxygen at the surface of Co_3O_4 , NiO , and CuO cannot be described by an equation of first order. Herefrom, the authors conclude that the surfaces of these catalysts are inhomogeneous. The isotopic exchange with Fe_2O_3 , however, fits an equation of first order. Fig. 6 shows $\log(1 - F)$ as a function of the time of exchange in the case of Fe_2O_3 . $F = (C_0 - C)/(C - C_\infty)$, where C_0 = concentration of O^{18} on the surface of the lattice, C = concentration of O^{18} in the gas, C_∞ = concentration of O^{18} on the surface of the lattice at equilibrium. Fig. 7 shows the changes in the activation energy of isotopic exchange along the

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surface. The reactivity of the oxides with respect to isotopic exchange changes in the same degree as their catalytic activity in hydrogen oxidation, i.e. $R_{Co_3O_4} > R_{NiO} > R_{CuO} > R_{Fe_2O_3} > R_{V_2O_5}$. The rates of

isotopic exchange and hydrogen oxidation are functions of the concentration of the oxygen adsorbed at the catalyst surfaces. S. M. Karpachev, A. M. Rozen and S. Z. Roginskiy are mentioned. There are 7 figures, 2 tables, and 14 references: 10 Soviet, 4 British, and 1 Japanese. X

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: September 26, 1960

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BORESKOV, G.K.; GORBUNOV, A.I.

Second International Congress on Catalysis in Paris. Kin. 1
kat. 1 no. 4:622-627 N-D '60. (MIRA 13:12)
(Catalysis--Congresses)

BORESKOV, G.K.; GORBUNOV, A.I., kand.khim.nauk

Second International Congress on Catalysis. Vest.AN SSSR 30 no.12:
49-54 D '60. (MIRA 13:12)

(Catalysis)

KASATKINA, L.A.; BORESKOV, G.K.; SOKOLOV, P.N.

Effect of potassium sulfate additions on the lability of oxygen in
vanadium pentoxide. Zhur. fiz. khim. 34 no.2:360-366 F '60.
(MIRA 14:7)

1. Khimiko-tekhnologicheskii institut im. D.I.Mendeleyeva, Moskva.
(Potassium sulfate) (Vanadium oxide) (Oxygen)

BORESKOV, G.K.; DZIS'KO, V.A.; PSIKUNOVA, Ye.M.; YUR'YEVA, T.M.

Silicon-boron-tungsten catalyst for the hydration of ethylene. Khim.
prom. no. 2:97-101 F '61. (MIRA 14:4)
(Ethylene) (Hydration) (Catalysts)

ANDREYEV, B.M.; BORESKOV, G.K.; KATAL'NIKOV, S.G.

Two-temperature method of separation of ions in a fixed ion-
exchanger bed. Khim.prom. no.6:389-393 Je '61. (MIRA 14:6)
(Ion exchange)

S/195/61/002/001/005/006
B101/B216

AUTHORS: Makarov, A. D., Boreskov, ~~G.~~ K., Dzis'ko, V. A.

TITLE: Chemical composition and catalytic properties of silicon-zirconium catalysts

PERIODICAL: Kinetika i kataliz, v. 2, no. 1, 1961, 84-93

TEXT: Basing on the fact that the catalytic properties of oxide mixtures are not additive, the present work studies the chemical nature and catalytic properties of silicon-zirconium catalysts, and whether this deviation from additivity is due to different acceleration of the individual reactions by the components (a view held, e.g., by B. B. Corson, et al., Ref. 1, see below), or to the chemical nature of the catalyst being changed by interaction between the two components. The following catalysts were prepared: (1) Silica gel by hydrolysis of the ethyl ester of orthosilicic acid, and ignition of the precipitate at 500°C; (2) ZrO_2 by precipitation of $ZrOCl_2$ with NH_3 , and ignition of the precipitate at 500°C; (3) mixed catalysts by joint precipitation of $ZrOCl_2$

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and the orthosilicic acid ester with NH_3 from aqueous-alcoholic solution, hydrolysis of the precipitate, and ignition; component ratios of the mixture and temperature of ignition were varied; (4) mechanical mixtures of the two components. The structure of the Si-Zr catalysts was examined by (A) X-ray analysis. Results obtained were: (a) ZrO_2 crystallizes at $400-450^\circ\text{C}$ in the tetragonal variety which at 500°C passes over to the monoclinic variety; (b) silica gel ignited at 1000°C is amorphous; (c) jointly precipitated Si-Zr mixtures containing up to 15% SiO_2 after ignition at 500°C exhibited the structure of a solid solution which decomposed after ignition at 1000°C and was re-formed when the temperature dropped below 1000°C . (B) Infrared spectrometric analysis in an IKS-2 (IKS-2) spectrometer in the range $2000-600\text{ cm}^{-1}$ gave the following results: (a) Silica gel shows absorption bands at 1170, 1100, and 810 cm^{-1} ; (b) ZrO_2 one at 735 cm^{-1} ; (c) the spectra of mechanical mixtures were additive; (d) samples obtained by joint precipitation had different spectra

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than the initial substances: the 735 and 810 cm^{-1} bands disappeared, and new bands appeared at 1060 and 960 cm^{-1} . The formation of an approximately equimolar chemical compound from the two components was established. ZrO_2 contained approximately 0.5% of structure water, silica gel, about 1%, and the jointly precipitated equimolar sample, 3%. Acidity was determined from the color change of an indicator, and the number of acid groups on the surface by titration with butyl amine. Silica gel and ZrO_2 are only slightly acidic, producing a color change of the acid indicator at $\text{pK} = 4$. The $\text{SiO}_2\cdot\text{ZrO}_2$ samples produced a color change at $\text{pK} = -8.2$. The catalytic activity was measured in a continuous-flow apparatus for the following reactions: (I) Preparation of divinyl from a mixture of 72.1% ethyl alcohol, 21.7% acetal, and 6.2% H_2O at 340°C . Table 1 shows the results obtained with the pure components and their mechanical mixtures, Table 2 the results for $\text{SiO}_2\cdot\text{ZrO}_2$ catalysts, and Table 3 those obtained with these catalysts after treatment with water vapor. (II) Decomposition of ethyl alcohol (Table 4) and isopropyl

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alcohol. (III) Condensation of acetal (Table 5). The results obtained were: (a) The non-additive catalytic properties of jointly precipitated Si-Zr catalysts were confirmed. This non-additivity is due to chemical combination of the components. (b) The number of acid groups on the surface of the equimolar sample and its catalytic activity decrease on heating to 800°C. In dehydration of ethyl alcohol, its catalytic activity is proportional to the acidity. (c) The condensation of acetal does not depend on the temperature to which the catalyst was heated. (d) The dehydration of aldol, as of alcohols, takes place at the OH groups on the catalyst surface and, therefore, decreases after ignition of the catalyst. The authors thank L. A. Ignat'yeva and Z. T. Orlova for taking and evaluating the spectra, and M. S. Borisova and M. V. Kostyukova for the acidity measurements. There are 6 figures, 5 tables, and 11 references: 5 Soviet-bloc and 6 non-Soviet-bloc. The references to English-language publications read as follows: B. B. Corson, H. E. Jones, Welling, Hincley, E. E. Stahly, Ind. Eng. Chem., 42, 359, 1950; R. E. Geller, Lang, J. Amer. Ceram. Soc., 32, (12 Part. II) 167, 1957.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
Card 4/11 (Physicochemical Institute imeni L. Ya. Karpov)

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SUBMITTED: November 12, 1960

Legend to Table 1: (1) sample number, (2) composition of the catalyst, (3) temperature at which 2-hr heat treatment was performed, °C, (4) yields of main reaction products, mole%; (a) ethylene, (b) hydrogen, (c) divinyl; (5) crystal structure, (6) mechanical mixture, (7) ditto, (8) monoclinic, (9) tetragonal, (10) amorphous, (11) traces.

Таблица 1

Разложение спирто-альдегидной смеси на ZrO_2 , SiO_2 и их механических смесях

(1) № образ- ца	(2) Состав катали- затора, мол. %		(3) Термическая обработка в течение 2 ча- сов при темпе- ратуре, °C	(4) Выход основных продуктов реакции, мол. %			h/S, $\frac{моль}{м^2 сек}$	Кристаллическая форма (5)
	ZrO_2	SiO_2		этилен (a)	водород (b)	дивинил (c)		
1	100	—	500	10,0	14,0	5,0	0,4	Моноклинная
2	100	—	450	8,0	13,0	7,0	0,6	Тетрагональная
3	100	—	300	8,5	11,9	6,0	0,5	Аморфная
4	—	100	500	12,0	2,0	21,0	0,08	Аморфная
5	31,4	68,6	(Механиче- ская смесь)	7,0	4,0	Следы	0,1	
6	66,2	33,8	То же	9,0	10,3	3,0	0,3	

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Legend to Table 3: (1) sample number, (2) composition of catalyst, mole%,
(3) yields of main reaction products, mole%; (a) ethylene, (b) divinyl;
(4) heat treatment; (c) temperature, (d) duration, hr, (5) preset
conditions for treatment with water vapor, (6) crystal structure,
(7) resinified, (8) ditto, (9) untreated, (10) solid solution, (11) amorphous,
(12) samples, (13) solid solution.

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Таблица 3

Влияние обработки водяным паром на избирательность действия кремнециркониевых катализаторов в реакции распада спирто-альдегидной смеси

① образцы №	② Состав катализатора, мол. %		③ Выход основных продуктов, реакц. мол. %		④ Термическая обработка		⑤ Условия обработки водяным паром		⑦ Кристаллическая форма
	ZrO ₂	SiO ₂	⑥ этилен	⑥ диоксины	температура, °C ⑥	время, час ⑥	температура, °C ⑥	время, час ⑥	
1	85,0	15,0	③ Осмоляется		1200 700	2 2	⑤ Не обработан		⑦ Твердый р-р
2	85,0	15,0	③ То же		1200 700	2 2	470	2	
3	50,0	50,0	5,0	07,0	500	2	⑤ Не обработан		⑦ Аморфная (образцы 3—11) ⑧
4	50,0	50,0	2,5	58,0	700	2	⑤ То же		
5	50,0	50,0	4,6	08,0	700	2	470	2	
6	10,0	90,0	5,0	06,0	500	2	⑤ Не обработан		
7	10,0	90,0	2,0	57,0	750	5	⑤ То же		
8	10,0	90,0	2,0	57,0	750	5	200	0	
9	10,0	90,0	2,5	60,0	750	5	330	2	
10	10,0	90,0	2,5	62,0	750	5	370	2	⑦ Аморфная + твердый р-р (образцы 12—14) ⑧
11	10,0	90,0	3,5	08,0	750	5	400	2	
12	10,0	90,0	2,0	50,0	850	10	⑤ Не обработан		
13	10,0	90,0	4,0	50,0	850	10	400	2	
14	10,0	90,0	4,0	56,0	850	10	470	2	

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Legend to Table 4: (1) sample number, (2) composition of catalyst, (3) heat treatment; (a) temperature, (b) duration, hr, (4) yields of main products, mole%, (c) ethylene + ether, (5) calculated for formation of chemical compound, (6) crystal structure, (7) mechanical mixture, (8) was not determined, (9) inactive, (10) monoclinic, (11) tetragonal, (12) amorphous, (13) samples, (14) solid solution, (15) well crystallized solid solution.

Таблица 4

Разложение этилового спирта при 340°

(1) № образца	(2) Состав катализатора, мол. %		(3) Термическая обработка		(4) Выход основных продуктов реакции, мол. %		(5) A/S-10 ³ моль м ³ ·сек	(6) A/S-10 ³ в расчете на химическое соединение, моль м ³ ·сек	(7) Кристаллическая форма
	ZrO ₂	SiO ₂	температура, °C (a)	время, час (b)	этилен+эфир (c)	H ₂			
1	100	—	500	2	58,0	33,0	4,2	—	(10) Моноклинная
2	100	—	450	2	57,0	32,0	4,5	—	(11) Тетрагональная
3	100	—	300	2	57,0	34,0	4,7	—	(12) Аморфная
4	31,9	68,1	(7) Механическая смесь		Не определялись		1,0	—	
5	—	100	500	2	100	—	0,7	—	

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Table 4
CONT.

6	92,5	7,5	425	2	100	—	8,4	5,5	Образцы 6—11: аморфные
7	85,0	15,0	435	2	100	—	18	6,0	
8	68,1	31,9	500	2	100	—	32	5,0	
9	50,0	50,0	500	2	100	—	53	5,3	
10	45,0	55,0	500	2	100	—	50	5,5	
11	10,0	90,0	500	2	100	—	10	5,0	
12	92,5	7,5	500	2	100	—	6,6	4,3	Образцы 12—17:
13	85,0	15,0	500	2	100	—	12	4,0	аморфные +
14	68,1	31,9	750	2	100	—	28	4,3	твердый р-р
15	50,0	50,0	800	3	100	—	38	3,8	
16	45,0	55,0	800	3	100	—	29	3,2	
17	10,0	90,0	850	10	100	—	7,0	3,5	
18	85,0	15,0	1200 700	2 2	Не активен (3)	—	—	—	Хорошо окри- сталлизованный твердый р-р

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Legend to Table 5: (1) sample number, (2) composition of samples, (3) heat treatment, (a) temperature, (b) duration, hr, (4) yield of croton aldehyde at various degrees of conversion, mole%, (5) crystal structure, (6) monoclinic, (7) amorphous, (8) solid solution.

Содержание таблицы. Результаты представлены в табл. 5.

Таблица 5.

Конденсация уксусного альдегида

(1) № образца	(2) Состав образцов, % мол.		(3) Термическая обработка		(4) Выход кротонового альдегида при различных степенях превращения, % мол.			(5) Кристаллическая форма
	ZrO ₂	SiO ₂	(a) температура, °C	(b) время, час	10	25	35	
1	100	—	500	2	100	87,0	50,0	8,25 (6) Моноклинная
2	—	100	500	2	100	91,0	78,0	0,4 (7) Аморфная (8)
3	10,0	90,0	500	2	100	92,0	80,0	0,8 Аморфная
4	10,0	90,0	850	10	100	80,0	—	9,2 (7) Твердый p-p+аморфная
5	55,0	45,0	500	2	100	94,0	78,0	49,0 Аморфная
6	85,0	15,0	500	2	—	70,0	62,0	61,0 (7) Твердый p-p+аморфная

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AUTHORS: Mishchenko, Yu. A., Boreskov, G. K., Kazanskiy, V. B.,
Pariyskiy, G. B.

TITLE: Effect of ionizing radiation on the catalytic and magnetic
properties of titanium dioxide

PERIODICAL: Kinetika i kataliz, v. 2, no. 2, 1961, 296

TEXT: Several papers published in the course of the last years studied the possibility of changing the catalytic properties of solids under the influence of high-energy radiation. Kohn and Taylor (Refs. 1, 2) observed a considerable effect of gamma and neutron radiations on the catalytic properties of Al_2O_3 and of catalysts on SiO_2 basis (Ref. 3) in the isotopic H - D exchange. It was the purpose of the present study to investigate the effect of gamma radiation on catalytic and magnetic properties of TiO_2 . The catalytic properties were studied by H - D exchange; the magnetic properties by electron paramagnetic resonance. The TiO_2 samples consisted of anatase with specific surface of the order $130 \text{ m}^2/\text{g}$. TiO_2 was heated to 500°C for several

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hours at 10^{-5} mm Hg prior to irradiation. The samples thus treated exhibited no marked catalytic properties at 0°C . They were now irradiated with gamma rays of Co^{60} in vacuo at the temperature of liquid nitrogen with 120 r/sec. The integral dose was about $1.7 \cdot 10^7$ r. The irradiated samples showed high catalytic activity at the temperature of liquid nitrogen. The catalytic activity was increased by at least 3-4 orders of magnitude. Heating of the irradiated samples to 0°C considerably decreased the catalytic activity. The constant of the reaction rate at 0°C 1 hr after thawing was by about two orders of magnitudes smaller than at the temperature of liquid nitrogen. The TiO_2 samples heated in vacuo at 500°C showed no signal when the epr spectrum was taken. At the temperature of liquid nitrogen, the samples irradiated gave a signal with well-resolved hyperfine structure, total width 400 oersteds, g factor approximately 2. The signal does not change if the sample is stored at the temperature of liquid nitrogen. Short heating to room temperature reduced intensity and changed the shape of the signal. When the samples were kept for 1 hr at room temperature the signal became stable. This parallelism in the changes of catalytic activity and epr signal was also observable in silica gel (Refs. 3-5) and Al_2O_3 (Refs. 2, 6). It

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may be concluded therefrom that irradiation gives rise to the formation of centers (defects, radicals) that cause the increased catalytic activity and the epr signal. The authors are now studying more thoroughly the changes of the epr signal and of the catalytic activity in the annealing of TiO_2 samples and under the action of various gases. References: 1) H. W. Taylor, E. H. Kohn, J. Amer. Chem. Soc., 79, 252, 1957; 2) E. H. Kohn, H. W. Taylor, J. Phys. Chem., 63, 500, 1959; 3) E. H. Kohn, H. W. Taylor, J. Phys. Chem., 63, 966, 1959; 4) E. H. Kohn, private communication on the 2nd International Congress of Catalysis, Paris, July 1960; 5) V. B. Kazanskiy, G. B. Pariyskiy, V. V. Voyevodskiy, Dokl. na II Vsesoyuznom soveshchanii po radiatsionnoy khimii (2nd All-Union Conference on Radiation Chemistry), October, 1960; 6) V. B. Kazanskiy, Yu. I. Pecherskaya, Zh. fiz. khim., 34, 477, 1960. [Abstracter's note: Complete translation of the original paper.] There are 6 references: 3 Soviet-bloc and 3 non-Soviet-bloc. The 3 references to English language publications are given in the text of the abstract.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: February 15, 1960

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5.4400

31090
S/195/61/002/004/005/008
E111/E585

AUTHORS: Keyyer, N.P., Boreskov, G.K., Rode, V.V.,
Terent'yev, A.P. and Rukhadze, Ye.G.
TITLE: Catalytic activity of organic semiconductors.
I. Polychelates

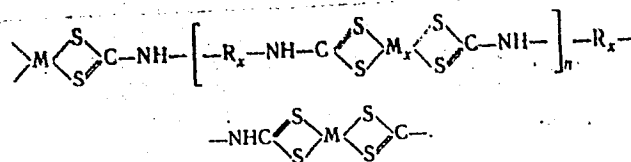
PERIODICAL: Kinetika i kataliz, v.2, no.4, 1961, 509-518

TEXT: The authors investigated various classes of organic polymers in order to establish the catalytic capacity of organic semiconductors and the relationship between their electrical conductivity and catalytic activity. The present work deals with polychelates of a given structure whose electrical conductivity varies by more than ten orders, depending on chemical composition. As regards chemical composition and structure the polychelates were of two types: 1) the sulphur atoms constitute the electron donor and, together with the metal, form the chelate group, which is connected with the radical by the =N-C group

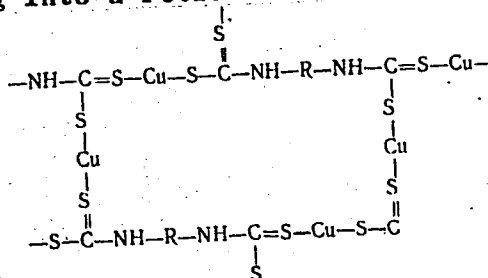
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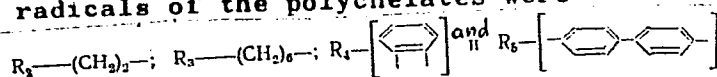


2) monovalent copper forms two coordination linear bonds
-S-Cu-S- evolving into a reticular structure



The organic radicals of the polychelates were

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The polychelates were synthesized through the interaction of equimolar aqueous solutions of the metal acetates with soda bis-dithiocarbamates $R_x(NHCSSNa)$: the molecular weight of the polychelates was 53×10^3 to 67×10^3 . The activity of twelve Ni, Cu, Co, Zn and Cd polychelates was studied in the decomposition reaction of 93% pure hydrazine hydrate at temperatures from 74 to 104°C. The Ni, Cu and Co polychelates displayed the highest catalytic activity, 100 times greater than that of NiO and NiS semiconductor catalysts; the Ni polychelate R_5Ni (type 1) had the highest activity and remained stable even after exposure to air; Zn and Cd polychelates displayed no activity at 104°C. The organic radicals had marked and varied effects on the catalytic activity of the polychelates. The catalytic activity of Ni polychelates was affected most; the highest activity was displayed by Ni polychelates with the organic radical R_5 and by Cu polychelates with R_2 ; the activity of the Co polychelates was affected only slightly by the organic radical. Although the results do not disclose any relation between the volume electrical conductivity $\sigma_{23}^\circ (\text{ohm} \cdot \text{cm})^{-1}$ and the catalytic activity of the polychelates, the

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pronounced effect of the organic radical on catalytic activity indicates a dependence of such activity on the electron state of the metal, which is conditioned by the donor groups and the organic radical entering into the composition of the polychelate. It is suggested that the electron effect on catalytic activity will be better understood when more is known about the regularities in the change of the surface electrical properties of the polychelates. Acknowledgments are expressed to Z. V. Zvonkova, V. M. Vozzhennikov and L. I. Badzhadze for data on the electrical conductivity of the samples and valuable advice. There are two tables, 6 figures and 10 Soviet-bloc references.

ASSOCIATION: Institut kataliza SO AN SSSR Khimicheskii fakul'tet
MGU (Institute of Catalysts SO AS USSR, Chemical
Faculty MGU)

SUBMITTED: May 22, 1961

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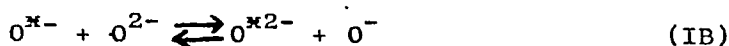
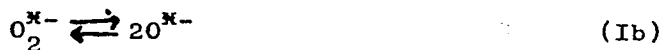
S/195/61/002/005/003/027
E111/E485

AUTHORS: Boreskov, G.K., Popovskiy, V.V.

TITLE: Mobility of the oxygen of solid oxides

PERIODICAL: Kinetika i kataliz, v.2, no.5, 1961, 657-667

TEXT: It is important for elucidating the reaction mechanism of oxide oxidation-reduction catalysts to investigate the reaction of oxides with oxygen. New opportunities for such investigation are provided by the use of the oxygen isotope, giving quantitative data on the oxygen mobility in surface and deep layers and its participation in catalyst-surface reactions. The authors discuss first mechanism and kinetics of exchange between molecular oxygen and oxide oxygen. The scheme of this exchange is given by



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Mobility of the oxygen ...

Adsorbed molecular or atomic oxygen ions are produced. The latter can exchange with oxide-lattice oxygen ions either with participation of oxygen defects (vacant oxygen sites in the lattice) or with definite displacement of crystal boundaries. The first case involves oxygen-atom displacement, the second does not. Assuming that displacements are equally probable over the whole surface and denoting by v the number of displacements in unit time, expressed in monolayers, and by n the number of displacements in time τ , the degree of exchange x , expressed in monolayers, is given by

$$x = \sum_{n=1}^{\infty} \frac{1}{(n-1)!} (v\tau)^n e^{-v\tau} \varphi(n). \quad (3)$$

Where

$$\varphi(n) = \frac{n + (n-1) + n(n-2) + n(n-3) + \frac{n(n-4)}{2!} (n-4) + \dots}{2^n \cdot n}. \quad (2)$$

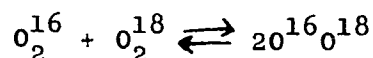
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Mobility of the oxygen ...

The mechanisms considered give different forms of x versus t curves and the authors give some examples taken from their previous work (Ref.4: Kinetika i kataliz, v.1, 1960, 566) for CuO , Co_3O_4 , NiO , Fe_2O_3 and V_2O_5 . The order of reaction with respect to oxygen for these oxides (except NiO) was found to be over 0.5. This indicates that the rate-controlling stage for exchange which is associated with the participation of molecular oxygen is either the oxygen adsorption or the conversion of the adsorbed molecular oxygen ions into the adsorbed atomic ions. A comparison of the rate of isotope exchange of the oxide oxygen with that of the homomolecular exchange of oxygen catalysed by oxygen



(from published data, e.g. Ref.5: A.P.Dzisyak, G.K.Boreskov, L.A.Kasatkina, V.Ye.Kochurikhin, Kinetika i kataliz, v.2, 1961, 386) gives further information on the nature of the rate-controlling stage. For Fe_2O_3 , Cr_2O_3 , NiO , V_2O_5 and V_2O_5 with alkali-metal sulphates as promoters, the rates of the two reactions, their

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Mobility of the oxygen ...

activation energy and order with respect to oxygen are the same. Consequently, either molecular-oxygen adsorption or conversion of adsorbed molecular into adsorbed atomic ions can be rate controlling. For MgO and ZnO no definite conclusions can be drawn. Since electron exchanges are involved, the Fermi level of the oxide should affect the isotope exchange but other factors tend to mark the effect. Only indirect evidence on this is available from variation of the stoichiometry of oxides by preliminary high-temperature treatment and influence on exchange rate of introduction of cations of a different valency into the oxide. At high temperatures the depth of exchange embraces a considerable part of the oxygen in the oxide crystals; the problem of allowing for oxygen diffusion inside the oxide is similar to that of the non-stationary heating of a solid immersed in a liquid; the authors used a published approximate equation (Ref.9: P.Carman, R.Haul, Proc. Roy. Soc., v.222A, 1954, 109) for treating their experimental results. At 800°C the diffusion coefficient values for oxygen in Co_3O_4 , CuO and Fe_2O_3 were 1.7×10^{-5} , 1.5×10^{-14} 2×10^{-15} (activation energies 76, 130 and 100 kcal/mol) respectively; that in V_2O_5 at 523 being 2×10^{-13} . The Card 4/7

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Mobility of the oxygen ...

comparison of mobility of surface oxygen is complicated by the order of reaction and activation energy being different for different oxides. Mobility can also depend on the preparation of the oxide. Published data show that the surface-oxygen mobility in fact varies within wide limits. The lowest exchange rate is possessed by oxides with cations having 0, 5 and 10 d-electrons, the lowest by those with an intermediate number of d-electrons. Differences in catalytic activity are less marked but similar in character (except for copper oxide). The data show that the escape energy of electrons is not the main factor determining the activation energy of exchange. The authors show that the exchange rate passes through a maximum, depending on the heat of the reaction



and that for oxides highly active in isotope exchange cations of different charges must be present during exchange. If the stationary oxygen content of the catalyst differs considerably from the equilibrium the direct relation between catalytic activity and Card 5/7

Mobility of the oxygen ...

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oxygen mobility, which otherwise prevails, can break down. The observed high rates of adsorbed and lattice oxygen transfer of oxygen-isotope exchange with oxides cast doubt on the idea that catalysed oxidizing reactions occur through reaction with adsorbed rather than lattice oxygen. The large variation in oxygen mobility of most oxides, even within the monolayer of surface ions suggests that the negligible transfer of oxide-catalyst oxygen into oxidation-reaction products should be attributed to the fact that only the small proportion of oxide-surface oxygen with a definite bonding energy participates in catalytic oxidation reactions. S.M.Karpacheva, A.M.Rozen, E.Kh.Yenikev and A.P.Dzisyak are mentioned in the article in connection with their contributions in this field. There are 6 figures, 2 tables and 16 references: 9 Soviet-bloc and 7 non-Soviet-bloc. The four most recent references to English language publications read as follows:
Ref.3: E.R.S.Winter, Adv. Catal., v.10, 1958, 196;
Ref.11: E.R.S.Winter, J. Chem. Soc., 1955, 3824;
Ref.14: D.Dowden, N.Mackenzie, B.Trappnell, Proc. Roy. Soc., v.237, 1956, 245; Ref.15: D.Dowden, Wals. Trans. of Second Internat. Congress on Catalysis, Paris, 1960.
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S/195/61/002/005/003/027
E111/E485

Mobility of the oxygen ...

ASSOCIATION: Fiziko-khimicheskiy institut im. L.Ya.Karpova
(Physico-Chemical Institute imeni L.Ya.Karpov)

X

Card 7/7

33481

S/195/61/002/005/006/027
E040/E485

5.2430

AUTHORS: Boreskov, G.K., Vasilevich, A.A.

TITLE: Effect of oxygen on the catalytic activity of
platinum films in isotopic hydrogen exchange reactions

PERIODICAL: Kinetika i kataliz, v.2, no.5, 1961, 679-683

TEXT: Using an apparatus described previously (Ref.4: Kinetika i kataliz, v.1, 1960, 69), the authors examined the effect of oxygen poisoning of Pt film catalyst in hydrogen adsorption, isotopic hydrogen exchange in molecular hydrogen and in isotopic exchange between chemisorbed and molecular hydrogen. Adsorption curves of hydrogen and oxygen at 90°K and at pressures varying from 1 to 4×10^{-2} mm Hg on freshly prepared Pt films showed that in both cases there is initially a rapid irreversible adsorption which is then followed by a slow and reversible one. The irreversibly adsorbed oxygen has a maximum cover corresponding to 67% of the available catalyst surface area. Tests on hydrogen adsorption by Pt films previously exposed to oxygen adsorptions of 3, 10 and 67% showed that oxygen behaves as a poison of Pt film with respect to the rapid initial adsorption of hydrogen but that the total

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Effect of oxygen on the catalytic ...

adsorption of hydrogen, i.e. the subsequent slow and reversible adsorption, increases. The mechanism of the process is such that, whereas at free points of the Pt film surface one hydrogen atom is adsorbed on each free point, two hydrogen atoms attach themselves to the surface points already occupied by one oxygen atom, presumably leading to the formation of 1 water molecule. The total quantity of hydrogen adsorbed on such oxygen-poisoned Pt films is $N = 1 + \theta_{O_2}$, where θ_{O_2} is the proportion of catalyst surface covered by oxygen atoms. Tests of tritium adsorption and isotopic hydrogen exchange with molecular hydrogen on oxygen-poisoned Pt film catalysts at 90°K and under hydrogen pressure of 0.1 mm Hg, showed that there is no change in the velocity of isotopic exchange at the points of the catalyst's surface not occupied by oxygen atoms, i.e. that oxygen has no effect on the catalytic behaviour in this respect of Pt films. This conclusion is further confirmed by test data obtained for isotopic exchange in molecular hydrogen at the temperatures of 78 and 90°K and at test pressures of 0.01, 0.1 and 1.0 mm Hg. However, at higher oxygen concentrations on the catalyst's surface, a drop was observed in the catalytic activity with rising

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Effect of oxygen on the catalytic ...

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E040/E485

concentration of oxygen atoms. There are 5 figures, 1 table and 4 references: 3 Soviet-bloc and 1 non-Soviet-bloc. The reference to an English language publication reads as follows:
Ref.3: O.Beeck, A.Smith, A.Wheeler, Proc. Roy. Soc., v.A177, 1940, 62.

ASSOCIATION: Fiziko-khimicheskiy institut im. L.Ya.Karpova
(Physico-Chemical Institute imeni L.Ya.Karpov)

Card 3/3

5.1190

33489

S/195/61/002/005/014/027

E111/E485

AUTHORS: Dzisyak, A.P., Boreskov, G.K., Kasatkina, L.A.,
Kochurikhin, V.Ye.

TITLE: Influence of additions of alkali-metal sulphates on
the catalytic properties of vanadium pentoxide in the
oxygen isotope-exchange reaction

PERIODICAL: Kinetika i kataliz, v.2, no.5, 1961, 727-731

TEXT: The authors report their investigation of the catalytic
activity of vanadium-pentoxide preparations, with additions of
analytical reagent purity sulphates of lithium, sodium, potassium,
rubidium or caesium (0.1 mol per mol of V_2O_5) as promoters, in the
temperature range 400 to 480°C and 40 mm Hg oxygen pressure.
For potassium sulphate mol fractions of 0.025 and 0.05 were also
tested. The method and apparatus used to study the homomolecular
reaction $O_2^{16} + O_2^{18} = 2O^{16}O^{18}$ were described in an earlier
paper (Ref.6: Kinetika i kataliz, v.2, 1961, 386). Furthermore,
the isotope exchange of each of the preparations with molecular
oxygen was studied when no homomolecular exchange was taking place.
Results are compared with those for pure vanadium pentoxide

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Influence of additions of alkali- ...

obtained previously (Ref.3: Kinetika i kataliz, v.1, 1960, 229 and Ref.6: as quoted above). Preliminary experiments had shown that both the rates R and K , respectively, of the catalyst/gas and the homo-molecular follow the first-order equation. When a catalyst enriched by a concentration of O^{18} equal to that in the gas is used, R can be calculated from

$$R = \frac{2,3}{TS} \frac{N_r \cdot N_r}{N_r + N_r} \lg \frac{C_{18}^0 - C_{18}^*}{C_{18} - C_{18}^*}, \quad (1)$$

and K from

$$K = \frac{2,3}{TS} \lg \frac{C_{34}^0 - C_{34}^*}{C_{34} - C_{34}^*} \quad (2)$$

In the case of simultaneous isotope exchange with the catalyst, the equation is

$$\frac{KS}{N_r} = \frac{C_{34}^0 - 2C_{18}^0 + 4C_{18}^* (C_{18}^0 - C_{18}^*) + 2(C_{18}^0 - C_{18}^*)^2 \frac{K-R}{K-2R}}{C_{34} - 2C_{18} + 4C_{18}^* (C_{18} - C_{18}^*) + 2(C_{18} - C_{18}^*)^2 \frac{K-R}{K-2R}} \quad (3)$$

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Influence of additions of alkali- ...

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In these equations R and K are in g/m^2 hour, N_T is the amount of oxygen in the gas phase, g ; N_T that in the catalyst, g ; S is the surface of the catalyst charge, m^2 ; τ is time, hours; C_{18}^0 , C_{18} and C_{18}^{∞} are the O_{18} proportion in the gas at the initial instant, at time τ and at equilibrium, respectively; C_{34}^0 , C_{34} and C_{34}^{∞} are the corresponding proportions of $\text{O}_{16}\text{O}_{18}$. The activation energy and rate values for the two reactions studied were found to be virtually the same. The rates were increased by the presence of the promoters, the order of promoter effectiveness (present in 0.1 mol-fraction concentration) increasing in the following order: $\text{Li}_2\text{SO}_4 < \text{Na}_2\text{SO}_4 < \text{K}_2\text{SO}_4 < \text{Rb}_2\text{SO}_4 < \text{Cs}_2\text{SO}_4$. The first increased the rate by 1.2, the last by about 100-fold. Even 0.025 mol of K_2SO_4 per mol pentoxide gave a considerable increase in both K and R , which were also found to be linearly related to the K_2SO_4 concentration. There are 3 figures, 2 tables and 7 references: 4 Soviet-bloc and 3 non-Soviet-bloc. The two references to English language publications read as follows: Ref.2: C.R.Kinney, J.Pincus, Ind. Eng. Chem., v.43, 1951, 2880; H.Hong, Chem. Ind., 1951, 872; Ref.4: Tandy. J. Appl. Chem., v.6, 1956, 68.

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Influence of additions of alkali- ...

S/195/61/002/005/014/027
E111/E485

ASSOCIATION: Moskovskiy khimiko-tekhnologicheskii institut
im. D.I. Mendeleeva (Moscow Chemical-technological
Institute im. D.I. Mendeleev)

X

Card 4/4

MARKINA, M.I.; BORESKOV, G.K.; IVANOVSKIY, F.P.; LYUDKOVSKAYA, B.G.

Catalytic activity of iron-chromium catalysts in the interaction
of carbon monoxide with water vapor. Kin.i kat. 2 no.6:867-871
N-D '61. (MIRA 14:12)

1. Gosudarstvennyy nauchno-issledovatel'skiy institut azotnoy
promyshlennosti.

(Carbon monoxide)
(Water vapor) (Catalysis)

BORESKOV, G. K.; CESALOVA, V. S.[Chesalova, V. S.]

Manufacture of industrial catalysts. Analele chimie 16 no.3:108-120
Jl-S '61.

(Chemical industries) (Catalysts)

BORESKOV, G.K.; SLIN'KO, M.G., kand.khim.nauk

Modeling of catalytic processes. Vest. AN SSSR 31 no.10:29-35
0 '61. (MIRA 14:9)

1. Chlen-korrespondent AN SSSR (for Boreskov).
(Catalysis)

S/076/61/035/001/013/022
B004/B060

AUTHORS: Popovskiy, V. V., Boreskov, G. K., and Muzykantov, V. S.
(Moscow)

TITLE: Study of the mechanism of hydrogen oxidation of cobaltous
cobaltic oxide by the oxygen isotope O^{18}

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 1, 1961, 192-197

TEXT: The authors studied the two possible oxidation processes on oxide catalysts: a) The oxidizing substances react with the oxygen of the catalyst; b) the oxygen of the catalyst does not participate in the reaction, but the oxidizing substances react with the oxygen of the gas phase, which is bound by chemisorption to the surface of the catalyst. This reaction mechanism has repeatedly been studied with the help of O^{18} . Isotopic exchange between molecular O_2 , oxidation product, and catalyst, however, may lead to errors. The purpose of the present work was to study the oxidation of H_2 on Co_3O_4 by means of O^{18} . The isotopes were analyzed with an MC-1 (MS-1) mass spectrometer. Co_3O_4 was obtained by heating

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Study of the mechanism of hydrogen ...

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B004/B060

cobalt nitrate to 400°C. Three specimens were prepared. Their specific surface was determined by adsorption of N₂ at a low temperature, and their catalytic activity W_c with respect to H₂ was determined in the oxygen excess (p_{O₂} ≈ 750 mm Hg, p_{H₂} ≤ 20 mm Hg). Table 1 gives the following values:

Catalyst	Specific surface, m ² /g	t, °C	W _{cH₂} = 10 ⁻⁷ mole H ₂ /cm ² .h
A	4.4	200	2.9 · 10 ⁻⁸
		150	6.2 · 10 ⁻⁸
		100	1.0 · 10 ⁻⁹
		75	5.0 · 10 ⁻¹⁰
B	7.7	100	8.8 · 10 ⁻¹⁰
		50	1.6 · 10 ⁻¹⁰
C	6.1	-	-

The authors studied a) the isotopic exchange between catalyst and atmospheric oxygen; b) the exchange between Co₃O₄ and water vapor in vacuo

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Study of the mechanism of hydrogen ...

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B004/B060

at 400°C for 4 hr; c) the exchange between water vapor and atmospheric oxygen; d) the participation of the catalyst oxygen. a) These experiments were made in a continuous-flow device at $p_{O_2} \sim 10$ mm Hg. A figure shows the fraction of exchanged oxygen ions of the catalyst surface at different temperatures. No exchange was observed at 75°C. The decreasing exchange rate indicates that the oxygen ions are heterogeneous. b) The water vapor was enriched in O^{18} . The isotope analysis of the water was carried out according to A. V. Trofimov (Ref. 9) by exchange with CO_2 and by a mass-spectrometric analysis of CO_2 . Exchange of 7, 30, and 20% was observed at 400, 75, and 50°C, respectively. Therefore, the oxygen exchange between water vapor and catalyst surface is to be taken into account. c) No exchange was observed at 75°C. d) This experiment was made at 75°C. In the experiments of the first series, the catalyst was enriched with O^{18} by isotopic exchange with water vapor at 400°C. The oxygen of H_2O contained approximately 16 at% O^{18} . Three experiments were made with the catalyst containing O^{18} , which was evacuated at 400°C for 4 hr: 1) oxidation of H_2 in O_2 excess at 75°C; 2) exchange reaction with the oxygen of H_2O ; ✓

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3) reduction with H_2 at 200-250°C. Results are collected in Table 2. In the second series, the catalyst contained natural oxygen, was evacuated at 400°C, treated with normal O_2 , which was then sucked off at 75°C. Subsequently, the device was filled with oxygen containing 4 at% O^{18} . In addition, the exchange between Co_3O_4 and water vapor was studied as in the first series. Results are presented in Table 3. The following conclusions were drawn from the results obtained: 1) At a temperature of 75°C, the major part of oxygen ions of the catalyst surface do not participate in the reaction. 2) After the catalyst has been heated to 400°C, only 2-20% of the oxygen ions of the catalyst surface participate in the reaction, while a treatment of the catalyst at 75°C increases this percentage to 13-39%. There are 1 figure, 3 tables, and 9 references: 8 Soviet-bloc and 1 non-Soviet-bloc.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: May 13, 1959

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S/076/61/035/006/004/013
B127/B203

AUTHORS: Boreskov, G. K. and Katal'nikov, S. G.

TITLE: Graphical method for determining the coefficient of isotope separation in stepwise compression of the mixture to be separated

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 6, 1961, 1240 - 1245

TEXT: The separation coefficient α of Rayleigh's formula was graphically determined. The individual process of separation is described by the

equilibrium formula $\alpha = \frac{y(1-x)}{y_0(1-y)}$ (5) and the material balance formula

$y_0 = \theta x + (1 - \theta)y$ (6). 1, θ and $(1 - \theta)$ are the numbers of moles of the substance to be separated in the initial, exhausted, and concentrated flow, respectively. ✓

respectively. $\frac{1}{1-\theta} = Z$ is the reduction of the flow of substance during separation. y_0, x, y are the molar parts of the isotope to be concentrated
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Graphical method for determining...

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B127/B203

in the respective flows. The joint solution of the balance equation and the equilibrium equation determines the concentrations x_i and y_i in the exhausted and concentrated flow of the individual steps of separation. For the graphical determination, the straight line corresponding to Eq. (5), as well as Eq. (6) transformed with $Z = \dots$, are plotted in a coordinate system. The tangent of the angle of inclination of this straight line indicates the reduction of flow of the given step. The intersection of the straight line $y_i = (1 - Z_i)x_i + Z_i y_{i-1}$ with the diagonal $y = x$ indicates the concentration of the respective isotope in the respective step. The equilibrium curve and the diagonal $y = x$ were plotted in the coordinates (y isotopic concentration in the concentrated part plotted on the ordinate, x concentration of the same isotope in the exhausted part plotted on the abscissa). From the point of the diagonal where $y = y_0$, a straight line with the inclination $(1 - Z_1)$ is drawn to the x -axis. The intersection with the equilibrium curve indicates the concentration of the isotope in the first step of separation. From this intersection, a parallel is drawn to the abscissa as far as the intersection with the diagonal. A straight line,

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tangent $(1 - Z_2)$, is passed through the new intersection as far as the intersection with the equilibrium curve, Figs. 1 and 2 show this on the example of isotopic exchange between BF_3 and the BF_3 -anisole complex. It is shown that the graphical determination permits a calculation of the loss of partially concentrated products. The amount of loss must be entered in the corresponding quantity Z_1 . For determining the separation coefficient, the method is first conducted with the value α determined by Rayleigh's formula. This hypothetical value α is then plotted on the abscissa, and the end concentration y_n , graphically predetermined for this value, on the ordinate. The intersection of the ordinate y_n with the curve obtained determines the required value α . The optimum distribution of substance reduction over the individual steps is calculated. In small intervals, the equilibrium curve can be substituted by the straight line $y = ax + b$ (10). The value x calculated from Eq. (10) and (6) gives

$$y_1 = Z_1 y_0 - (Z_1 - 1) \frac{y_1 - b}{a} \quad (11)$$

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The same is made with the second step. Thus,

$$y_2 = \frac{Za^2y_0 + Zab + Zb + b(a-1) - b(Z_1 + Z/Z_1)}{Z + (Z_1 + Z/Z_1)(a-1) + (a-1)^2} \quad (14)$$

This equation is differentiated; it yields $Z_2^2 = Z$, and confirms that $Z_1 = Z_2$. The authors refer to a paper by G. M. Panchenkov et al. (Zh. fiz. khimii, 31, 1951, 1957), as well as by Ye. M. Kuznetsova, A. V. Makarov, G. M. Panchenkov (Zh. fiz. khimii, 32, 2641, 1958). There are 4 figures and 9 references: 3 Soviet-bloc and 6 non-Soviet-bloc. The three most important references to English-language publications read as follows: T. Y. Taylor, H. C. Urey, J. Chem. Phys., 6, 429, 1939, A. A. Palko et al., J. Chem. Phys. 28, 211, 1958; *ibid.*, 29, 1187, 1959.

ASSOCIATION: Moskovskiy khimiko-tekhnologicheskii institut im. D. I. Mendeleyeva (Moscow Institut of Chemical Technology imeni D. I. Mendeleyev)

SUBMITTED: September 9, 1959.
Card 4/6

BORESKOV, G.K.; GORBUNOV, A.I.

Effect of chromium additions to a nickel skeleton catalyst
on the rate of isotope exchange in molecular nitrogen. Zhur.
fiz.khim. 35 no.9:2071-2077 '61. (MIRA 14:10)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova i Moskovskiy
khimiko-tekhnologicheskii institut imeni D.I. Mendeleyeva.
(Nitrogen—Isotopes) (Nickel)

S/020/61/136/001/026/037
B004/B056

AUTHORS: ~~Borisev, G. K.~~, Corresponding Member AS USSR, Dzis'ko, V.A.,
and Tyulikova, T. Ya.

TITLE: The Effect of Water and Oxygen on the Polymerization of
Ethylene Upon Chromium Oxide Catalysts

PERIODICAL: Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 1,
pp. 125-128

TEXT: Greatly differing data of the efficiency of chromium oxide catalysts in ethylene polymerization (Refs. 1-3) gave rise to the present paper. Impurities are assumed to have an effect. The present paper gives an account on the effect of water and oxygen on polymerization. The catalyst was made of aluminosilicate carrier, bulk weight 0.43, pore radius 40-60 Å, surface 300 m²/g. This base was impregnated by chromic acid, dried at 110°C, heated to 250°C, and activated by 4 hours' heating to 400°C at 10⁻³ torr. The finished catalyst contained 5% CrO₃. Primarily, experiments were made with extremely pure ethylene. Purity was attained by

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The Effect of Water and Oxygen on the Polymerization of Ethylene Upon Chromium Oxide Catalysts

S/020/61/136/001/026/037
B004/B056

passing C_2H_4 at a pressure of 50 atm through carbon filters, through a column with nickel-chromium catalyst (for O_2 removal), and through columns with active Al_2O_3 (removal of water). The solvents, BP-1 (BR-1)-type gasoline, cyclohexane or heptane were also freed from water and oxygen by Al_2O_3 and blowing-through of N_2 . Purified C_2H_4 contained about 5 parts-per-million O_2 and H_2O , the solvents contained about 5 parts-per-million H_2O . Polymerization took place in a stainless steel autoclave of 1 liter volume. Special measures (breakoffski for catalyst-containing ampoule, magnetic mixer) prevented access of impurities during the reaction. Processing was as follows: Heating of autoclave to $200^\circ C$, evacuation for two hours, cooling down to $100^\circ C$, repeated blowing-through of pure C_2H_4 . Subsequently, 300 g of purified solvent were pressed into the autoclave by means of N_2 , followed by C_2H_4 addition up to a pressure of 35 atm. Curves I of Fig. 2 (polymer yield versus catalyst concentration) and Fig. 3

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. The Effect of Water and Oxygen on the Polymerization of Ethylene Upon Chromium Oxide Catalysts

S/020/61/136/001/026/037
B004/B056

(efficiency of the catalyst versus its concentration) illustrate the results obtained with pure C_2H_4 . Curves II were obtained for higher water content (20 parts-per-million). Fig. 4 shows the effect of oxygen upon the efficiency of the catalyst. It is assumed that the impurities are adsorbed on the catalyst and thus obstruct its activity centers. The authors thank B. A. Lipkind, Chief Engineer of the Gor'kovskaya baza NIINP (Gor'kiy Base of the Scientific Research Institute of the Petroleum Industry) for supplying the carrier samples. There are 4 figures and 3 references: 2 Soviet and 1 Belgian.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of Physical Chemistry imeni L. Ya. Karpov)

SUBMITTED: August 17, 1960

Legend to Fig. 2: I: Water content in the solvent 5 parts-per-million.
II: Water content in the solvent 20 parts-per-million; a) content of catalyst in the solvent, b) polymer yield.

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BORESKOV, G.K.; SLIN'KO, M.G.

Theory of similitude principles applied to heterogeneous
catalysis. Khim.prom. no.6:418-424 Je '62. (MIRA 15:11)
(Catalysis) (Chemical models)

35064

S/195/62/003/001/005/010
EO71/E156

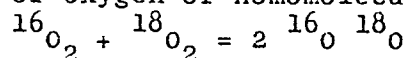
J.1190

AUTHORS: Dzisyak, A.P., Borcskov, G.K., and Kasatkina, L.A.

TITLE: An investigation of homomolecular oxygen exchange on the metal oxides of the fourth period

PERIODICAL: Kinetika i kataliz, v.3, no.1, 1962, 81-90

TEXT: The object of the work is a systematic investigation of homomolecular exchange of oxygen on oxides of transitional metals of the fourth period in order to elucidate the mechanism of the intermediate interaction of molecular oxygen with oxides and the establishment of the relationship between the catalytic activity and chemical nature of an oxide. In the reported part of the work the apparent activation energy and the order in respect of oxygen of homomolecular oxygen exchange



on the above oxides were determined. The study was carried out in a static circulation apparatus described earlier (Ref.5: Kinetika i kataliz, v.2, 1961, 386, 727) by the present authors and V.Ye. Kochurikhin. The starting non-equilibrium mixtures
Card 1/4

X

An investigation of homomolecular ... S/195/62/003/001/005/010
E071/E136

of isotopic oxygen molecules were prepared by mixing enriched oxygen with a concentration of ^{18}O of 37% with natural oxygen in a ratio of 1:1. The control of all types of oxygen molecules was carried out with a mass spectrometer MW-1305 (MI-1305). The relative accuracy of measuring the concentration was $\pm 1\%$. A sample of oxide charged into the reaction vessel was treated for 8 hours in a vacuo (10^{-5} mm Hg) at 400°C . Subsequently the isotopic exchange of the oxide investigated with molecular oxygen was carried out. To remove the distorting influence of isotopic exchange, all samples were kept in oxygen with the initial concentration of heavy isotope until cessation of the exchange. Moreover, before each measurement the catalyst specimen was retained in the initial mixture to establish a stationary composition of the oxide. Due to this treatment the content of ^{18}O in gas during homomolecular exchange reaction remained constant. The preparation of oxides was described previously (Ref.8: V.V. Popovskiy, G.K. Boreskov, Sb. Problemy kinetiki i kataliza, v.10, Izd-vo AN SSSR, M., 1960, p.67 (Symposium: Problems of Kinetics and Catalysis, v.10, edited by Card 2/4

X

An investigation of homomolecular ... S/195/62/003/001/005/010
E071/E136

AS USSR, p.67). The powders were pressed into tablets and crushed into grains of 3 mm. Specific surface of oxides was determined by low temperature nitrogen absorption. It was established that the activity of the oxides investigated in respect of homomolecular exchanges increases in the following order:

$TiO_2 < V_2O_5 < Cr_2O_3 < ZnO < Fe_2O_3 < CuO = NiO < MnO_2 < Co_3O_4$.

The velocity of homomolecular exchange is equal to the initial velocity of isotopic exchange between molecular oxygen and oxygen of the respective oxide. The following stages of the reaction are necessary for the homomolecular exchange: 1) adsorption - desorption of molecular oxygen with its dissociation into atoms or ions; 2) migration of adsorbed atoms or ions along the surface. For isotopic exchange between oxide and gas a stage of substitution of an ion in the lattice with adsorbed oxygen is necessary. Two possible mechanisms can explain the equality of velocities of homomolecular and isotopic exchange. (1) Adsorption - desorption of molecular oxygen takes place at a much lower velocity than the exchange of adsorbed atoms or ions of oxygen with ions of lattice oxygen. In this case the ratio of

Card 3/4

X

An investigation of homomolecular ... S/195/62/003/001/005/010
E071/E136

concentration of molecules $^{16}\text{O } ^{18}\text{O}$ to $^{18}\text{O } ^{18}\text{O}$ in the gas should remain constant. (2) Oxygen is adsorbed with dissociation into atoms or ions but the desorption, due to a low concentration or mobility of these atoms or ions, takes place mainly on their recombination into molecules with ions of lattice oxygen. In this case the ratio of $^{16}\text{O } ^{18}\text{O}$ to $^{18}\text{O } ^{18}\text{O}$ should increase in the course of the reaction. Previous experiments (Ref.5) with V_2O_5 and V_2O_5 with additions of alkali sulphates favour the first mechanism. However, these results cannot be transferred to other oxides without special experiments. There are 5 figures, and 3 tables.

ASSOCIATION: Moskovskiy khimiko-tekhnologicheskii institut im.
D.I. Mendeleeva
(Moscow Institute of Chemical Technology imeni
D.I. Mendeleev)

SUBMITTED: November 15, 1961

Card 4/4

X

BORESKOV, G.K.; VASILEVICH, L.A.; GUR'YANOVA, R.N.; KERNERMAN, V.Sh.;
SLIN'KO, M.G.; FILIPPOVA, A.G.; CHESNOKOV, B.B.

Oxidation of ethylene in a fluidized bed of a catalyst. Kin. i
kat. 3 no.2:214-220 Mr-Ap '62. (MIRA 15:11)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR i Fiziko-khimi-
cheskiy institut imeni L.Ya.Karpova.
(Ethylene) (Oxidation) (Fluidization)

BORESKOV, G.K.

Quantitative characteristics of catalytic activity. Kin.i kat.
3 no.4:470-480 J1-Ag '62. (MIRA 15:8)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR.
(Catalysis)

BORESKOV, G.K.

Some problems of heterogeneous catalysis. *Kin.i kat.* 3 no.5:
633-642 S-O '62. (MIRA 16:1)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR.
(Catalysis)

KEYYER, N.P.; BORESKOV, G.K.; RUBTSOVA, L.F.; RUKHADZE, Ye.G.

Catalytic activity of organic polymers. Part 3: Some regularities of catalytic activity on the chelate polymers of various chemical composition and structure. *Kin.i kat.* 3 no.5:680-690 S-O '62.
(MIRA 16:1)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR i Moskovskiy gosudarstvennyy universitet imeni Lomonosova.
(Chelates) (Catalysis)

S/195/62/003/005/007/007
E202/E492

AUTHORS: Shendrik, M.N., Boreskov, G.K., Goryainova, R.M.,
Slin'ko, M.G.

TITLE: Method of investigating catalysts undergoing rapid
activity changes during the process of reaction

PERIODICAL: Kinetika i kataliz, v.3, no.5, 1962, 797-799

TEXT: A laboratory scale installation for studying circulation
of reaction mixture with a continuous flow of catalyst through
the reactor is briefly described. The method is used in the
dehydrogenation of butane. The circulating system was kept at
a constant pressure of 30 mm Hg. The reaction mixture was
continuously removed from the reactor and its volume analysed
chromatographically. Precipitation of carbon on the catalyst was
also determined. It was shown that with the reaction gas
circulation of 200 to 270 litres/hour, and the dehydrogenation
reaction at 550 to 590°C, the time of residence of the pseudo
liquefied catalyst in the reactor for a period of 11 to 20 min,
equilibrium was reached within 4 to 6 hours and its stability
retained as long as the volume of the catalyst permitted. The
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Method of investigating

S/195/62/003/005/007/007
E202/E492

activity of the catalyst expressed as litres ($C_4H_8 + C_4H_6$)/litres of catalyst·hour was measured by changing the residence time of catalyst in the reactor. Details of five runs with butane feed ranging from 6.6 to 12.7 litres/hour are given. There are 1 figure and 1 table.

ASSOCIATION: Giprokauchuk Institut kataliza SO AN SSSR
(Giprokauchuk Institute of Catalysis SO AS USSR)

SUBMITTED: June 1, 1962

Card 2/2

S/020/62/143/005/014/018
B101/B110

AUTHORS: Yermakov, Yu. I., Boreskov, G. K., Corresponding Member
AS USSR, Dzis'ko, V. A., and Ivanova, L. I.

TITLE: Low-temperature polymerization of ethylene on chromium oxide
catalyst

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 143, no. 5, 1962,
1139-1141

TEXT: The polymerization of ethylene at 75°C, i.e., below the m.p. of the polymer, on a chromium oxide catalyst, whose preparation has been described earlier (DAN, 136, no. 1, 125 (1961)), is discussed. The experiments were made with high-purity C₂H₄ (1-2 ppm O₂, 3 ppm H₂O) in purified n-heptane at constant pressure (5-15 atm). The following results were obtained (Fig. 1): (1) an induction period was observed (30-150 min), which was shorter at higher pressure and higher concentration of the catalyst; (2) after the induction period the reaction rate remained constant for a long time (at low catalyst concentration up to

Card 1/3

Low-temperature polymerization ...

S/020/62/143/005/014/018
B101/B110

20 hrs); (3) the polymer consisted of 0.2 to 3 mm large granulae; (4) the initial grains of the catalyst had a size of 0.5 to 1 mm. Catalyst particles of 1-10 μ were found on the surface (not in the bulk) of the polymer grains; (5) a threshold concentration of the catalyst exists below which there is no polymerization. Hence no polymerization occurred with 0.0274% catalyst in the solvent, and a slight polymerization with 0.0325%; (6) the activity, A, of the catalyst, depends on the pressure, P; $A = aP^n$ (a, n = constants). At < 9 atm, $n \sim 2$, at 11-15 atm, $n \sim 3$; (7) the molecular weight, MW, is independent of the catalyst concentration, but depends on P: at 9 atm, the MW was 110,000-125,000, at 15 atm, the MW was 400,000-600,000; (8) a maximum yield (1800 g polyethylene per g catalyst) was obtained at 15 atm and 0.0520% catalyst concentration. There are 4 figures and 1 table.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: January 11, 1962

Card 2/3

Low-temperature polymerization ...

S/020/62/143/005/014/018
B101/B110

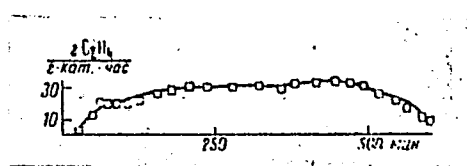


Fig. 1: kinetic curve of C_2H_4 polymerization at 9 atm, $75^\circ C$, catalyst concentration 0.336%. Legend: abscissa time, min; ordinate $g C_2H_4 / g \text{ catalyst} \cdot hr$.

Card 3/3

385M
S/020/62/144/005/011/017
B124/B138

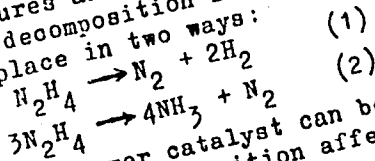
5.3750 11.2205
11.1325

AUTHORS: Borekov, G. K., Corresponding Member, AS USSR, Keyyer, N. P.,
Rubtsova, L. F., and Rukhadze, Ye. G.

TITLE:

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 144, no. 5, 1962, 1069-1072

TEXT: The article covers studies of the effect of the following: on the catalytic activity of chelate polymers the decomposition of hydrazine, the metal component, the chemical composition of the atoms of the admixtures in the chelate center, and the organic portion of the polymer in the main or side-chains. Structures and compositions of the polymers are given in Table 1. Hydrazine decomposition is sensitive to the electron state of the contact, and takes place in two ways:



The selectivity of a polymer catalyst can be assessed from the way in which its structure and chemical composition affect the direction of hydrazine

Ca:

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18 3

S/020/62/144/005/011/017
B124/B138

APPROVED FOR RELEASE: 06/09/2000

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decomposition of isopropyl alcohol was also studied. No oxidation took place on the activity of polychelates of copper with chelate centers of different compositions: $\text{Cu}(\text{N},\text{S}) > \text{Cu}(\text{S},\text{S}) > \text{Cu}(\text{N},\text{O}) > \text{Cu}(\text{O},\text{O})$. The catalytic activity of chelate polymers is twice as high as that of inorganic copper semiconductors. The same was found for the selectivity of the investigated. Fig. 3 shows the dependence of the selectivity of the copper polychelates on their chemical composition and structure. It is concluded that the catalytic activity and selectivity of a polychelate depends on: 1) the metal entering into the polychelate; 2) the nature of the organic part of the polymer. There is thus an analogy between the rules governing the catalytic properties of these polymers and that of ferments. There are 3 figures and 2 tables. The English-language reference is: E. Leslie, Orgel, An Introduction to Transition-Metal Chemistry. Ligand-Field Theory, London, 1960.

Card 2/18

3

Catalytic properties of...

S/020/62/144/005/011/017
B124/B138

ASSOCIATION: Institut kataliza Sibirskogo otdeleniya Akademii nauk SSSR
Novosibirsk (Institute of Catalysis of the Siberian
Department of the Academy of Sciences USSR, Novosibirsk).
Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED: December 8, 1961

Table 1. Study of chelate polymers.

Legend: (A) polymer; (B) Organic compound on the basis of which the
polychelate was isolated; (D) Chelate center; (E) Composition of
polychelate; (F) Sodium bis-di-thiocarbamate; (G) α -thioalkylpyridine
amidodiphenyl; (J) 2b Rubianic acid; (K) Poly-(4,4' bis)- α -thio-2,6-lutidine
amidodiphenyl; (L) 5,5'-methylene-bis-salicylaldehyde; (M) 3b Diacetyl
resorcinol; (P) 4b Dinitrosoresorcinol.

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S/020/62/145/004/022/024
B101/B138

AUTHORS: Kuchayev, V. L., and Boreskov, G. K., Corresponding Member
AS USSR

TITLE: Catalysis and adsorption of hydrogen on germanium films

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 145, no. 4, 1962, 853-856

TEXT: The authors tested the data of Y. L. Sandler, M. Gazith (J. Phys. Chem., 63, 1095 (1959)) on the catalytic activity of sputtered Ge films. Special devices (Fig. 1) prevented contact between the Ge and the tungsten wire coil and eliminated its catalytic effect by immersion in liquid Ga. The ampoule was heated to 450°C and evacuated to $3 \cdot 10^{-7}$ mm Hg, before sputtering on the Ge. This was done by passing a current (13.5 a) through the W coil, with the ampoule immersed in liquid nitrogen. Catalytic activity and rate of H_2 adsorption were measured according to Kinetika i kataliz, 1, no. 3, 356 (1960). Results: (1) The specific rate of H_2 adsorption was $(29 - 56) \cdot 10^{-14}$ mole/cm²·sec·mm Hg. (2) The catalytic activity of H - D exchange at 100°C was less than $1 \cdot 10^{-15}$ mole/cm²·sec,

Card 1/2 Z

Catalysis and adsorption of ...

S/020/62/145/004/022/024
B101/B138

i.e., in agreement with K. Tamaru, M. Boudart (Adv. in Cat., 9, 699 (1957)) and five times less than the values of Sandler and Gazith. This is attributed to the fact that these scientists had not eliminated the catalytic activity of the W coil. There are 3 figures and 1 table. ✓

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: April 29, 1962

Fig. 1. (A) Reaction vessel for studying the rate of H_2 adsorption on Ge films. (1) ampoule; (2) Mo lead-in, 3.5 mm diam; (3) coil of 0.5 mm W wire; (4) graphite crucible; (5) glass tube; (6) ~0.1 g Ge; (7) iron wire which is removed with a magnet. (B) Device for immersing the W coil in liquid Ga. (1) ampoule; (2) iron bar with which the test tube (3) containing liquid Ga (4) is raised toward the W coil; (5) copper wire for fixing the device in raised position; (6) glass rod operated by iron bar (7) sealed in glass, for removing air bubbles from (3).

Card 2/2 2

YERMAKOV, Yu.I.; BORESKOV, G.K.; DZIS'KO, V.A.; IVANOVA, L.I.; TRIFONOV,
A.S. ~~XXXXXXXXXXXXXX~~

Polymerization of ethylene on a chromia catalyst without a solvent. Khim.prom. no.7:496-498 J1 '63. (MIRA 16:9)

BORESKOV, G.K.; DZISYAK, A.P.; KASATKINA, L.A.

Homomolecular oxygen exchange studied on oxides of metals
of the fourth period. Part 2: Catalytic activity and bond
energy of oxygen in oxides. Kin. i kat. 4 no.3:388-394
My--Je '63. (MIRA 16:7)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR i Moskovskiy
khimiko-tekhnologicheskoy institut imeni Mendeleyeva.
(Metallic oxides) (Chemical bonds)
(Catalysis)

L 10702-63

ACCESSION NR: AP3002024

EWB(j)/EPF(c)/RWT(m)/BDS--ASD--PC-1/Pr-1--RM/11/

5/0195/63/004/003/0492/0494

AUTHOR: Bukanayeva, F. M.; Boreakov, G. K.; Dzila'ko, V. A.

TITLE: Investigation of the chromium oxide catalyst for high polymerization of ethylene

SOURCE: Kinetika i kataliz, v. 4, no. 3, 1963, 492-494

TOPIC TAGS: chromium oxide, CrO sub 3 catalyst, polyethylene, catalyst carrier, activated CrO sub 3

ABSTRACT: The conditions for activating CrO sub 3 for production of polyethylene were investigated: CrO sub 3 concentration, nature of carrier, reactivity with solvents. Pure CrO sub 3 is completely dissociated at 400 degrees, while with 5% CrO sub 3 on silica gel, Al or Mg silicate at the same temperature 90% is still in the hexavalent state and at 800 degrees, 30% of the Cr is still hexavalent. Increasing CrO sub 3 from 5 to 20% on the carrier decreases its activity, apparently because of decrease in dispersibility. CrO sub 3 on a carrier is most rapidly reduced in methycyclohexane, moderately reduced by cyclohexane and n-heptane and least in benzene; pure CrO sub 3 does not react with heptane due to formation of layer Cr sub 2 O sub 3. When activated CrO sub 3 catalyst is treated with solvent,

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L 10702-63

ACCESSION NR: AP3002024

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polymerization induction period is prolonged (to provide for desorption of solvent-reaction products from catalyst surface), but catalyst activity is actually increased. EPR spectra of activated and of activated cyclohexane-treated catalyst show same signal intensity, presuming same amount of reduction to Cr sup +5. Hence solvent does not participate in formation of active component of the catalyst; catalyst activation is determined by surface combination of the Cr with the carrier. "EPR spectra were taken at the Institut khimicheskoy fiziki AN SSSR (Institute of Chemical Physics, Academy of Sciences SSSR." Orig. art. has: 3 figures and 3 tables.

ASSOCIATION: Institut kataliza SO AN SSSR (Catalyst Institute, Siberian Department of the Academy of Sciences SSSR)

SUBMITTED: 30Jan63

DATE ACQ: 12Jul63

ENCL: 00

SUB CODE: 00

NO REF SOV: 005

OTHER: 001

ja/ *[signature]*

Card 2/2

BORESKOV, G.K.; SLINKO, M.G. [Slin'ko, M.G.]

Application of the methods of similitude theory in heterogenous catalysis. Analele chimie 18 no.2:176-189 Ap-Je '63.

BORESKOV, G.K.

Problems of heterogenous catalysis. Analele chimie 18 no.3:143-153 J1-S '63.

BORESKOV, G.K.; GORBUNOV, A.I.

Preparation of metallic catalysts as vacuum condensed films on
a finely disperse carrier. Zhur. fiz. khim. 37 no.12:2728-
2733 D '63. (MIRA 17:1)

1. Fiziko-khimicheskiy institut imeni L.Ya. Karpova.

BORESKOV, G.K.; GORGORAKI, V.I.; KASATKINA, L.A.

Reaction involved in a homomolecular exchange of oxygen
between ZnO and NiO at room temperature. Dokl. AN SSSR 150
no.3:570-573 My '63. (MIRA 16:6)

1. Moskovskiy khimiko-tekhnologicheskii institut im. D.I.
Mendeleeva. 2. Chlen-korrespondent AN SSSR (for Boreskov).
(Oxygen) (Metallic oxides)
(Chemical reaction, Rate of)

BORESKOV, G.K.; DZIS'KO, V.A.; YEMEL'YANOVA, V.M.; PECHERSKAYA, Yu.I.;
KAZANSKIY, V.B.

Catalytic activity and electron paramagnetic spectra of
molybdenum oxide catalysts for the polymerization of ethylene.
Dokl. AN SSSR 150 no.4:829-832 Je '63. (MIRA 16:6)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR i Institut
khimicheskoy fiziki AN SSSR. 2. Chlen-korrespondent AN SSSR
(for Boreskov).

(Molybdenum catalysts--Spectra)
(Polymerization)

KHASIN, A.V.; BORESKOV, G.K.

Isotopic exchange of oxygen on platinum films. Dokl. AN SSSR
152 no.6:1387-1390 0 '63. (MIRA 16:11)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR. 2. Chlen-
korrespondent AN SSSR (for Borenskov).

BORESKOV, Georgiy Konstantinovich

"Theoretical bases of selection, preparation and use of industrial catalysis".

Report to be submitted at the Third International Congress on Catalysis, (IUPAC), Amsterdam, Netherlands, 20-25 Jul 64.

BORESKOV, G.K.; SLIN'KO, M.G.

Basic principles of the modeling and optimalization of chemical
reactors. Khim.prom. no.1:22-29 Ja '64. (MIRA 17:2)

ACCESSION NR: AP4016519

S/0195/64/005/001/0120/0127

AUTHOR: Gorgoraki, V. I.; Boreskov, G. K.; Kasatkina, L.A.;
Sokolovskiy, V. D.

TITLE: Homomolecular exchange of oxygen on zinc oxide at low temperatures

SOURCE: Kinetika i kataliz, v. 5, no. 1, 1964, 120-127

TOPIC TAGS: zinc oxide, zinc oxide catalyst, homomolecular exchange, catalytic action, oxygen 16, oxygen 18

ABSTRACT: This study was prompted to determine the causes of catalytic action of ZnO. To comprehend the causes, one should understand the nature and character of bonds formed by the dissociative chemisorption of oxygen on the surface of oxides. The exchange reaction at room temperature not only affects ZnO (an n-type semiconductor), but also NiO (a p-type semiconductor). The reaction was investigated by means of homomolecular exchange of oxygen isotopes

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ACCESSION NR: AP4016519

$O_2^{16} + O_2^{18} = 2O^{16}O^{18}$ on ZnO calcined at 850C, and then rapidly cooled to 25, -63 and -194C. At the two latter temperatures the exchange rate is close to that at 425C, and the product has a stable activity. The apparent activation energy at these two temperatures is 0.18 kcal/mol. The exchange rate in the initial moment at 25C is many times greater than in the 425-500C range. In oxygen atmosphere there is a rapid deactivation (5-6 hrs) of ZnO, but deactivated ZnO can be reactivated with zinc vapor. The catalytic activity of ZnO is caused by zinc excess. This can be the intermodular zinc of the surface oxide layer, i.e., Zn dissolved in ZnO or zinc formed on the surface oxide layer and adsorbed by same. Orig. art. has: 2 figures and 2 tables.

ASSOCIATION: Moskovskiy khimiko-tekhnologicheskii institut imeni D. I. Mendeleeva (Moscow Chemical Engineering Institute)

SUBMITTED: 24Apr 63

DATE ACQ: 18Mar64

ENCL: 00

SUB CODE: CH

NO REF SOV: 002

OTHER: 005

Card 2/2

BORELSKOV, G.K.

Simulation of chemical processes. Vest. AN SSSR 34 no.5,
47-56 My '64. (MIRA 12:16)

1. Chlen-korrespondent AN SSSR.

ACCESSION NR: AP4011443

S/0076/64/038/001/0115/0124

AUTHORS: Andreyev, B. M. (Moscow); Boreskov, G. K. (Moscow)

TITLE: Bi-temperature separation in systems with solid phase

SOURCE: Zhurnal fiz,khim, v. 38, no. 1, 1964, 115-124

TOPIC TAGS: bi-temperature separation, binary mixtures, counterflow, two-phase exchange, linear velocity, moving zones, temperature zones, cold columns, hot columns

ABSTRACT: A study has been made of the method of binary mixture separation which is a new version of the bi-temperature method. The latter is used in a counterflow two-phase exchange in gas-liquid systems, and it facilitates the separation process in systems with a solid phase. The first series of tests involved the use of a separating column consisting of four sections, and the column employed in the second series was made up of 10 such sections. The relationship between the degree of separation and the flow ratio in the hot and cold column was investigated. A characteristic feature of the bi-temperature method is the relationship between the dis-

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ACCESSION NR: AP4011443

tribution of the component concentrations in the column and the flow ratio. The continuous method of analyzing the solution coming out of any of the separating sections makes it possible to determine the concentration by use of the column as the movement of the temperature zones is accompanied by appropriate shifts in the concentration contours. The maximum degree of separation was achieved when the hot and cold zones were of the same height. It took only a few hours to achieve a stationary state of the concentrations. The separating efficiency is determined by the linear velocity of the solution in the ion-exchange column, and the test results indicate a high degree of such efficiency. Orig. art. has: 12 Figures, 8 Formulas and 2 Tables.

ASSOCIATION: Moskovskiy khimiko-tekhnologicheskii institut imeni D. I. Mendeleeva (The Moscow Mendeleev Institute of chemical technology).

SUBMITTED: 16Mar63

DATE ACQ: 14Feb64

ENCL: 00

SUB CODE: CH

NR REF SOV: 005

OTHER: 000

Card 2/2

BORESKOV, G.K.; MATVEYEV, K.I.; OSIPOV, A.M.; BUKHROYAROV, P.F.

Flow-through circulation apparatus for studying reactions of gaseous substances in the presence of a liquid catalyst. Zhur.fiz.khim. 38 no.8:2104-2106 Ag '64. (MIRA 18:1)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR.

BORESKOV, G.K.; SHCHEKOKHIKHIN, Yu.M.; MAKAROV, A.D.; FILIMONOV, V.N.

Use of infrared absorption spectra in studying the structure of surface compounds formed during adsorption of ethanol on γ -oxide of aluminum. Dokl. AN SSSR 156 no. 4:901-904 Je '64.
(MIRA 17:6)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR i Leningradskiy gosudarstvennyy universitet im. A.A.Zhdanova. 2. Chlen-korrespondent AN SSSR (for Boreskov).

L 6716-65 EWT(m)/EPF(c)/EWP(j)/T/EWP(a)/EWP(b) Pe-L/Pr-L RAEM(i)/SSD/ 7/
 AS(mp)-2/RAEM(c)/ASD(a)-5/AFWL/ESD(gs)/ESD(t) JD/RM 69
 ACCESSION NR: AP4042209 S/0020/64/157/002/0384/0387

AUTHOR: Borakov, G. K.; Kazanskiy, V. B.; Mishchenko, Yu. A.; Pariyskiy, G. B.

TITLE: The nature of active centers in hydrogen isotope exchange reaction on irradiated silica gel. 27

SOURCE: AN SSSR, Doklady*, v. 157, no. 2, 1964, 384-387

TOPIC TAGS: hydrogen, deuterium, silica gel, electron paramagnetic resonance, spectrophotometry, isotope exchange, irreversible adsorption, gamma irradiation, hydrogen deuterium exchange reaction

ABSTRACT: The purpose of this work was to study the nature of F-centers in irradiated silica gel by optical methods and by radiospectroscopy, and to determine their role in irreversible adsorption of hydrogen and catalytic activity. Prior to irradiation silica gel samples were kept under a vacuum for 24 hours at 400, 500 or 600 C and at residual pressure of 10^{-5} - 10^{-6} mm. After pretreatment samples were irradiated with γ -rays from a Co^{60} source at liquid nitrogen temperature and at room temperature. The irradiation dose varied from 2×10^5 to 2×10^7 r. The catalytic activity of silica gel in H_2 - D_2 exchange reaction was measured at

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L 6716-65

ACCESSION NR: AP4042209

equimolar content of the mixture at 77°C K and 0.7 mm pressure. The isotope composition of hydrogen in the course of reaction was measured by means of the electrical conductivity of the mixture. Adsorption measurements were done at room temperature and 5×10^{-3} to 5 mm pressure. The absorption in diffuse scattered light was measured at room temperature with an SF-4 spectrophotometer (see fig. 1 of the enclosure) modified for this purpose according to Ye. I. Kotov (Optika i Spektroskopiya, 3, 92, 1959). EPR spectra were measured with microwave spectrometer EPR-2 at 77°C K (see fig. 2 of the enclosure). During irreversible adsorption of hydrogen molecules (above 100°C), they dissociate and electrons are transferred from hydrogen atoms to holes with consequential reduction of acid centers in the nonirradiated silica gel. Since this process required energy of activation it does not proceed at liquid nitrogen temperature. The isotope exchange of hydrogen and deuterium at -196°C occurs on the very same centers, however, adsorption is not accompanied by dissociation but it merely results in weakening of bonds between atoms which constitute these centers. At elevation of temperature the rate of dissociation type of adsorption increases which results in vanishing of active centers. The energy nonuniformity of the radiation produced defects leads to the fact that even at room temperature part of them remains intact, undisturbed by the irreversible adsorption of hydrogen. These defects are catalytically active

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centers. Orig. art. has: 2 tables and 3 figures.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics, Academy of Sciences SSSR); Institut kataliza Sibirskogo otdeleniya Akademii nauk SSSR (Institute of Catalysis, Siberian Branch, Academy of Sciences SSSR)

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3/5

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ENCLOSURE: 01

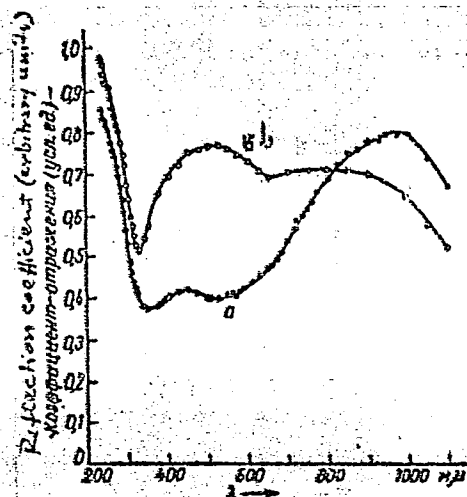


Fig. 1. Optical spectra of silica gel before (a) and after (b) adsorption of hydrogen at room temperature.

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ENCLOSURE: 02

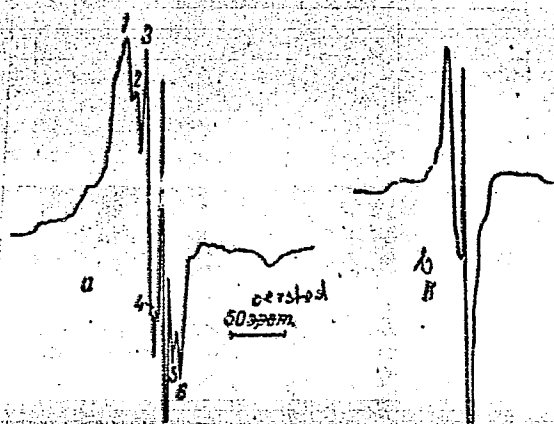


Fig. 2. EPR spectra of irradiated silica gel before (a) and after (b) adsorption of hydrogen.

Card 4/5

BORESKOV, G.K.; MUZYKANTOV, V.S.; POPOVSKIY, V.V.; GOL'DSHTEIN, N.D.

Isotope oxygen exchange in the system aluminum γ -oxide -
molecular oxygen. Dokl. AN SSSR 159 no.6:1354-1356 D '64
(MIRA 18:1)

1. Institut kataliza Sibirskogo otdeleniya AN SSSR. 2. Chlen-
korrespondent AN SSSR (for Boreskov).

L 35549-65 EMT(m)/EPF(c)/EMP(j)/T Pc-h/Pr-h RM

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AUTHORS: Yermakov, Yu. I.; Dzis'ko, V. A.; Tyulikova, T. Ya.; Trifonov, A. S.;
Boreskov, G. K.

TITLE: A method for producing polyethylene. Class 39, No. 168883

SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 5, 1968, 71

TOPIC TAGS: polyethylene, polymerization, inert solvent

ABSTRACT: This Author Certificate presents a method for producing polyethylene by low-temperature polymerization of ethylene with a chrome-chrome oxide catalyst in an environment of inert solvent at low pressures. In order to obtain polyethylene with a low ash content, an inert solvent containing water is used for the enviroing medium. Water is introduced into the solvent in amounts of 20-32 parts per million.

ASSOCIATION: none

SUBMITTED: 29Mar62

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OTHER: 000

Card 1/1

NEIDUMOVA, Ye.S.; BORESKOV, G.K.; SLIN'KO, M.G.

Kinetics of isotope exchange between hydrogen and water vapors on nickel catalysts. Part 1: Effect of transport processes on the reaction rate. Kin. i kat. 6 no.1:65-73 Ja-F '65. (MIRA 18:6)

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